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Ab initio vibrational–rotational spectrum of potassium cyanide: KCN

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Dynamical calculations are performed on an *ab initio* potential energy surface for KCN. Approximate variational solutions of the vibrational Eckart hamiltonian are presented for several states. Fundamental vibrations are found to lie at 302·7 cm^{-1} and 119·7 cm^{-1}. An effective rotational hamiltonian is solved for several vibrational states allowing vibrational assignments to be made to the observed rotational spectrum.

1. INTRODUCTION

Recent work, both experimental [1, 2] and theoretical [3, 4], has shown the equilibrium geometry of KCN to be triangular. This, at first, surprising result makes the dynamics of the KCN molecule of special interest. First, the flatness of the potential energy surface for the bending motion of the K around the CN makes the molecule especially floppy in this coordinate. The low barrier, 504 cm^{-1} predicted by [3] for the linear isocyanide structure, should lead to vibrations of very large amplitude after only a few states. The word *polytopic* has been coined [5] to describe projected motions of this type in the LiCN molecule. The vibrational states lying below this barrier can also be expected to be of large amplitude.

Secondly, triangular KCN is an asymmetric top. This leads to a complicated rotational spectrum which has been much studied experimentally [1, 2, 6, 7]. At the temperatures at which these esperiments are conducted, 600–900° C, many vibrational states are significantly populated. This further complicates the observed rotational spectrum. Rotational transitions have been observed from at least 11 different vibrations states [2], but as yet no definite assignments have been made for anything but the ground vibrational state. For this state alone the spectrum is well characterized [2].

The experimental data on the vibrational spectrum of KCN is sketchy and contradictory. The only direct measurement of the gas phase vibrational spectrum of KCN [8] observed just one transition (at 207 cm^{-1}) between 200 cm^{-1} and the C–N stretching mode at 2158 cm^{-1}. This does not agree with any of the levels reported by Ismail *et al.* [9] from matrix isolation studies who found the 3 fundamentals at 288 cm^{-1}, 139 cm^{-1} and 2050 cm^{-1}. We

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note that their $\omega_1 \simeq 2\omega_2$ and therefore Fermi resonance effects are to be expected. An estimate of the inertial defect from the ground state rotational spectrum places ω_2 at about 157 cm^{-1} [2].

The aim of this work is to compute a vibrational–rotational spectrum for KCN from first principles. It is hoped that a more definite vibrational spectrum can be produced and some more positive assignments made to the rotational spectrum of the vibrational excited states. KCN also provides an interesting test of the theoretical methods used to tackle ro-vibrational problems. First, the high amplitude bending motions can be expected to present special difficulties not encountered in more rigid molecules previously investigated using variational methods, a review of which is provided by Carney *et al.* [10]. Secondly, the large energy separation between the lowest two fundamentals and the CN stretch suggests that an approximate theoretical separation might also be possible.

In this paper we employ a method based on the Eckart hamiltonian [11] which was developed by Whitehead and Handy [12]. The potential energy surface used is the one calculated *ab initio* at the SCF level by Wormer and Tennyson (WT) [3].

For molecules with small amplitude internal motion, use of the Eckart hamiltonian ensures the best possible separation of vibrational and rotational motion. This separation involves the neglect of Coriolis terms between different vibrational states. Although these terms may be significant for a molecule undergoing large amplitude vibrations, Holmgren *et al.* [13] found similar Coriolis terms to be small for the van der Waals complex ArHCl. KCN is considerably less floppy than ArHCl in its low lying vibrational states and in § 4 we demonstrate that these off-diagonal Coriolis terms are indeed small.

In this case it is possible to consider the vibrational problem separately from the rotational problem, thus greatly reducing the dimensions of the secular equations to be solved. In the Whitehead–Handy approach it is assumed that the vibrational wavefunction can be expanded as a sum of products of harmonic basis functions and the rotational wavefunction as a sum of spherical harmonics. The Whitehead–Handy method has previously been applied to several non-linear tightly bound molecules, with well defined equilibrium geometries, such as H_2O [12], SO_2 [12] and H_2CO [14] with satisfactory results. Recently, Bartholomae *et al.* [15] have applied the Whitehead–Handy method to CH_2^+, which has a low barrier to inversion. They found that the method worked well if they used a specially constructed basis which avoided singularities in the region of linear geometries.

In § 2 of this paper we give detail of the method used to solve the ro-vibrational problem. Section 3 presents solutions to the vibrational hamiltonian with $J=0$. These are used in § 4 to solve an effective rotational–vibrational problem.

2. METHOD

Assuming, as usual, that nuclear and electronic motions may be separated, then the hamiltonian for the vibration–rotation motion may be written as

$$\hat{H} = \tfrac{1}{2} \sum_{\alpha\beta} (\Pi_\alpha - \pi_\alpha)\mu_{\alpha\beta}(\Pi_\beta - \pi_\beta) + \tfrac{1}{2} \sum_k P_k{}^2 - \frac{\hbar^2}{8} \sum_\alpha \mu_{\alpha\alpha} + V \tag{1}$$

where Greek letters run over cartesian coordinates and Roman over normal coordinates. This form of the hamiltonian, which contains only nuclear variables, was derived by Watson [16] from the hamiltonian Darling and Dennison [17] developed from the original formulation of Eckart [11].

In (1) $\boldsymbol{\mu}$ is an effective inverse inertia tensor, Π_α is a component of the negative total angular momentum operator and π_α is a component of the Coriolis operator

$$\pi_\alpha = \sum_{kl} \epsilon_{kl}{}^\alpha \, Q_k P_l, \quad P_l = \frac{h}{i} \frac{\partial}{\partial Q_l}. \tag{2}$$

V is the potential for the nuclear motion in the effective field of the electrons.

A more detailed account of the construction and significance of the terms in (1) is given by Watson [16]. An account of how to construct the proper normal coordinates Q_k for a general molecule can be found in Wilson *et al.* [18]. For present purposes, however, it is sufficient to note that if the internal motions represented by the Q_k are very small, then $\boldsymbol{\mu}$ becomes approximately the inverse of $\mathbf{I}_0$, the equilibrium geometry inertia tensor, and the Coriolis term becomes approximately zero.

In this case H becomes H^0 and (1) separates into two parts

$$H^0 = H_{\mathrm{rot}}{}^0 + H_{\mathrm{vib}}{}^0 \tag{3}$$

with

$$H_{\mathrm{rot}}{}^0 = \tfrac{1}{2} \sum_{\alpha\beta} (\mathbf{I}_0{}^{-1})_{\alpha\beta} \Pi_\alpha \Pi_\beta \tag{4}$$

and

$$H_{\mathrm{vib}}{}^0 = \tfrac{1}{2} \sum_k P_k{}^2 - \frac{\hbar^2}{8} \sum_\alpha (\mathbf{I}_0{}^{-1})_{\alpha\alpha} + V. \tag{5}$$

In the absence of magnetic fields, H^0 has solutions of the form

$$\Psi_J{}^0(\mathbf{Q}, \boldsymbol{\phi}) = \Phi^0(\mathbf{Q}) \sum_{K=-J}^{+J} d_K{}^0 |JK\rangle, \tag{6}$$

where $|JK\rangle$ is an angular momentum eigenfunction involving the Euler angle $\boldsymbol{\phi}$, and Φ^0 is a solution of the problem

$$H_{\mathrm{vib}}{}^0 \, \Phi^0 = E_{\mathrm{vib}}{}^0 \, \Phi^0. \tag{7}$$

The coefficients $d_K{}^0$ of the angular momentum eigenfunctions are determined by solving the secular problem specified by $H_{\mathrm{rot}}{}^0$ acting on the manifold of angular momentum functions of a given J. The complete sum-function so determined is often called a rigid asymmetric-top function.

This analysis suggests that, for reasonably small internal motions, H can approximately be separated into two parts

$$H_{\mathrm{vib}} = \tfrac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} \pi_\alpha \pi_\beta + \tfrac{1}{2} \sum_k P_k{}^2 - \frac{\hbar^2}{8} \sum_\alpha \mu_{\alpha\alpha} + V \tag{8}$$

and

$$H_{\mathrm{rot-vib}} = \tfrac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} \Pi_\alpha \Pi_\beta - \sum_{\alpha\beta} \mu_{\alpha\beta} \Pi_\alpha \pi_\beta. \tag{9}$$

By solving the problem associated with H_{vib}, a manifold of vibrational functions Φ_n can be calculated. A suitable manifold for the full problem can thus be constructed as a direct product of these Φ_n and the complete set of $|JK\rangle$ for a given J. $H_{\mathrm{rot-vib}}$ then operates on the full manifold coupling its members. It is convenient to think of the operation of $H_{\mathrm{rot-vib}}$ in terms of the operation of an *effective* rotational hamiltonian whose elements are

$$H_{\mathrm{rot}}{}^{mn} = \tfrac{1}{2}\sum_{\alpha\beta} \langle \Phi_m|\mu_{\alpha\beta}|\Phi_n\rangle \Pi_\alpha \Pi_\beta - \sum_{\alpha\beta} \langle \Phi_m|\mu_{\alpha\beta}\pi_\beta|\Phi_n\rangle \Pi_\alpha \tag{10}$$

and which operates on the angular momentum functions only. In (10) the integrals are over the vibrational coordinates Q_k only and Φ_n is a vibrational wavefunction. If it is the case that, for any chosen vibrational state, the off-diagonal ($m \neq n$) contribution of these integrals to H^{mn} is small compared with their diagonal ($m = n$) contribution, then to a good approximation, the coupling between different vibrational functions may be neglected. In this case a suitable wavefunction has the form

$$\Psi_J(\mathbf{Q}, \boldsymbol{\phi}) = \Phi_n(\mathbf{Q}) \sum_{K=-J}^{+J} d_K |JK\rangle \tag{11}$$

where Φ_n is the chosen vibrational function. The d_K are determined by solving the secular problem over the $|JK\rangle$ with $H_{\mathrm{rot}}{}^{nn}$ for an appropriate chosen n.

In this context we note that the operator

$$\sum_\beta \mu_{\alpha\beta}\pi_\beta \tag{12}$$

is hermitian and purely imaginary. Thus, as the Φ_n are real, the second integral in (10) vanishes for $m = n$. It is thus required, for (11) to be a valid approximation, that the $m = n$ case of the first integral in (10) dominates *both* integrals that arise when $m \neq n$.

In the present work the potential used in H_{vib} was derived from the *ab initio* SCF calculations of WT [3] and the actual hypersurface was obtained by an accurate fit to the calculated points. Previous *ab initio* calculations with the Whitehead–Handy method [12, 15] used *ab initio* potential points precalculated to a chosen integration scheme. Whilst attractive, as any loss of accuracy due to the fitting is eliminated, this approach has two practical drawbacks. First, a knowledge of the surface is required before it is computed in order to select an equilibrium geometry and a suitable range of integration points. Secondly, if high order numerical integration is required many more potential points are needed, in our case 256 as against the 24 actually used in the surface fit. As calculating potential points is very expensive in computer time this is a severe caveat.

The surface of WT [3] is not a full surface for KCN, but has one internal coordinate, the CN bond length, frozen. A realistic representation of this coordinate would not be possible without inclusion of electron correlation. However, it is not possible to solve the Watson hamiltonian (1) with an arbitrary internal coordinate frozen. This point will be developed in the next section.

3. VIBRATIONAL PROBLEM

The potential energy surface of WT [3] is expanded in three internal coordinates, R, θ and r (frozen), as defined in figure 1. In order to generate

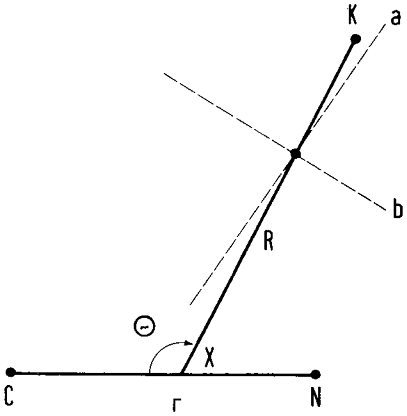


Figure 1. Coordinates system, R, θ and r, for KCN. X denotes the centre of nuclear mass of $^{12}C-^{14}N$, a and b schematically represent the principle axes of inertia, with c perpendicular to the plane of the paper, and a and R are very nearly coincident.

normal coordinates for the solution of the vibrational hamiltonian (8) it is necessary to satisfy the Eckart conditions [11]. It is then possible to solve the hamiltonian (8) in less than ($3N$-6) dimensions by freezing certain of these normal coordinates, as has been done recently for CO_2 and SO_2 by Clary [19]. For infinitessimal displacements from equilibrium our internal coordinates have the necessary properties, but not for real displacements. Thus it is not possible to freeze an arbitrary internal coordinate. This means that although the C–N stretch is well separated in energy from the other fundamentals, it must be included in the solution of (8).

To the surface of WT we thus added a harmonic term in r_{CN} with force constant $k=0{\cdot}172\ \mu N\ Å^{-1}$ which is typical of observed CN values [18], p. 175. This force constant leads to a fundamental frequency of 2129·7 cm^{-1} for the CN stretch, intermediate to those observed for KCN [8, 9]. We aim to show that the final solution of the vibrational problem for the other two fundamentals is insensitive to this choice. This leads to potentials which can be expressed as

$$V(R,\theta,r)=\sum_{l=0}^{6} V_l(R)P_l(\cos\theta)+\tfrac{1}{2}k(r-r_e)^2 \tag{13}$$

where $V_l(R)$ is given in reference [3] and r_e was taken as 1·157 Å, the value of WT.

Vibrational basis functions were taken as products of gaussian weighted Hermite polynomials for each normal coordinate

$$\Psi(n_1,n_2,n_3)=H_{n_1}(\bar{Q}_1)H_{n_2}(\bar{Q}_2)H_{n_3}(\bar{Q}_3)\exp\left[-\tfrac{1}{2}(\bar{Q}_1^2+\bar{Q}_2^2+\bar{Q}_3^2)\right] \tag{14}$$

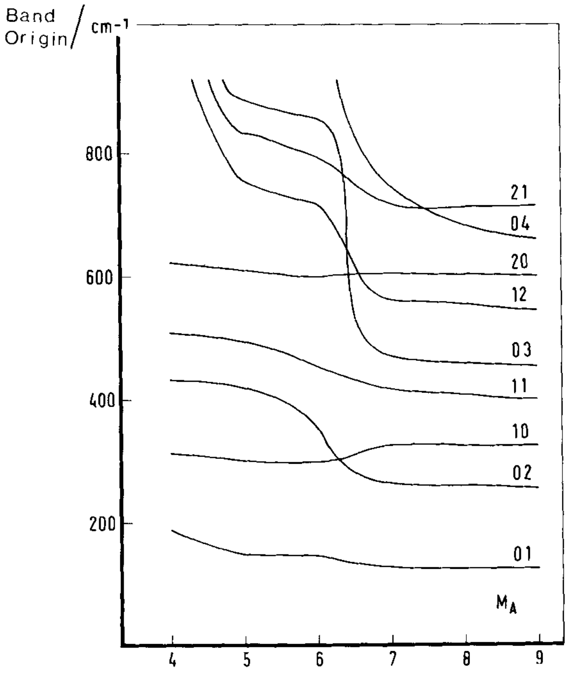
$$\bar{Q}_k=\left(\frac{\omega_k}{\hbar}\right)^{1/2}Q_k \tag{15}$$

where ω_k are fundamental frequencies given by solution of the harmonic problem. The normal coordinates Q_k were obtained in cartesian form using programs developed by Schachtschneider [20].

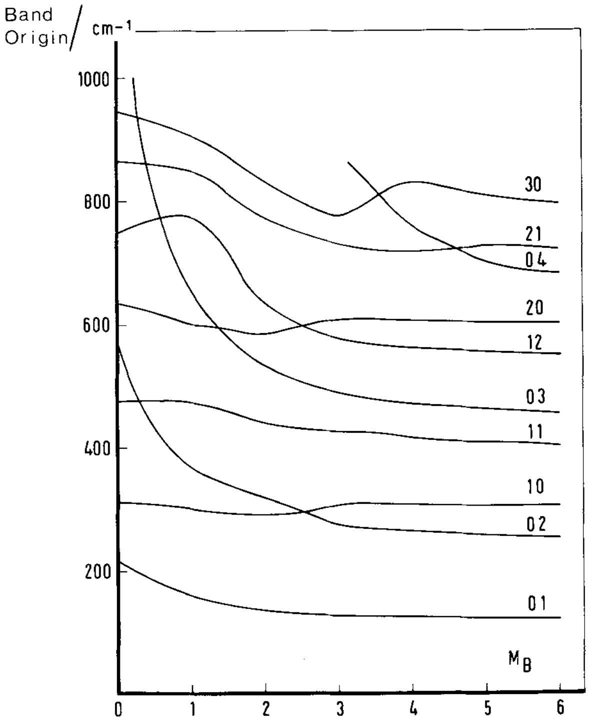
As in [12] matrix elements were evaluated using a product of one dimensional Gauss–Hermite integration schemes with the points distribution weighted by the harmonic frequency of the fundamentals. Each numerical integration point is thus defined in terms of weighted normal coordinates Q_k. One gets the current cartesian geometry from these by applying the transformation generated by the Schachtschneider programs [20] ; this geometry is used to give an inverse inertia tensor for the current point. The potential was evaluated at each integration point in the body-fixed coordinates R, r and $\cos\theta$, which can be obtained simply from the cartesian geometry.

As comparatively large basis sets (up to 385 functions) were used and, since only the lowest vibrational states were of interest, we used the method of Shavitt *et al.* [21] to give the first few vibrational states. This proved more economic in both storage and computer time than diagonalizing the whole matrix, especially as vectors from a previous run often provide a good starting point for the cyclic diagonalization.

In order to solve the vibrational problem it is necessary to obtain convergence with both basis set size and integration point grid. To this end we divided our normal coordinates into two types : A comprising Q_1 and Q_2 which can approximately be identified with the K–CN stretch and bend respectively ; B comprising Q_3 or the C–N stretch. What we require is convergence for the fundamentals and low-lying states of type A. Basis functions for type B with $n_3 > 0$ are included solely to remove the effects of the CN stretch included in the basis functions of type A. Convergence with M_A and M_B was tested separately



(*a*)



(*b*)

Figure 2. Convergence of band origins with increasing basis set size. (*a*) Increasing M_A with $M_B = 4$. (*b*) Increasing M_B with $M_A = 7$. States are identified by their major harmonic components with $n_3 = 0$. The ground 00 state is taken as the energy zero.

where

$$M_A \geq n_1 + n_2, \quad M_B \geq n_3. \tag{16}$$

This leads to a basis of $(M_A+1)(M_A+2)(M_B+1)/2$ functions. Figures 2 (*a*) and (*b*) show the convergence of the band origins with increasing M_A and M_B respectively. Excited states are identified with the harmonic basis function having the largest component ($n_3 = 0$ for all low lying states). For states with $n_2 > 2$ this labelling is necessarily rather arbitrary as the anharmonicity in the angular potential strongly mixes the harmonic basis. Figure 2 shows several state crossings. As all vibrational states are of A' symmetry, these should strictly be depicted as avoided crossings. However as M_A and M_B are both integer variables it is pointless to speculate what form the curves take for non-integer values, hence we have linked directly points with similar harmonic components. Figure 2 suggests that our basis set is well converged for the ground and first seven excited states for $M_A = 9$ and $M_B = 6$. Next we test the convergence of our numerical integrals. We compared calculations for $M_A = 8$, $M_B = 6$ and a 16, 16, 8 point gaussian integration scheme for modes 1, 2 and 3 respectively with ones using 18, 18, 6 and 16, 16, 10 schemes. None of the band origins were changed by more than 0·02 cm^{-1}. This shows that we have none of the problems with near linear geometries encountered by Bartholomae *et al.* [15]. In their case the problem is probably exacerbated by studying a triatomic containing two hydrogen atoms. As a final check on the convergence of the basis, we tested the effect of altering the empirical CN force constant included in our potential. An increase of 10 per cent lifts the harmonic CN stretch frequency by 104 cm^{-1}; for a calculation with $M_A=8$, $M_B=6$ it only raises the other two fundamentals by about 0·5 cm^{-1}. We thus feel that our calculations are well converged. Table 1 presents results for an $M_A=9$, $M_B=6$ calculation.

Table 1. Lowest 9 vibrational states for calculation with $M_A=9$, $M_B=6$. Energies are relative to the ground state; states are labelled by the harmonic basis functions which have a coefficient greater than 0·40 in absolute value. $n_3=0$ for all components given.

State	Energy/cm^{-1}	Harmonic basis function	Coefficient	Harmonic basis function	Coefficient
		n_1 n_2		n_1 n_2	
1	0·0	0 0	0·98		
2	119·7	0 1	0·87		
3	241·9	0 2	0·68		
4	302·7	1 0	0·92		
5	382·9	0 3	0·46	1 1	0·41
6	438·6	1 1	0·74		
7	524·0	1 2	0·57		
8	588·3	2 0	0·69		
9	616·7	2 0	−0·45	1 2	0·45

The minimum of the potential of WT lies at −39086·1 cm^{-1} relative to a zero at fully separated K^+ and CN^- ions. Our ground vibrational state has an energy of −37798·3 cm^{-1} including 1064·9 cm^{-1} zero point energy from the harmonic CN^- potential. The zero point energy for the other two fundamentals is thus 222·9 cm^{-1} which is higher than that given by halving the sum of the two fundamental energies, 211·2 cm^{-1}. However, as there is significant interaction between the 02 and 10 states, the latter method of deriving zero point energies is not very reliable.

WT predicts a barrier to inversion of 503·9 cm^{-1} for an isocyanide geometry. This places the vibrational state 438·6 cm^{-1} above the ground state at about the same height as the barrier, when allowance is made for the zero point energy of the bending mode. Bending vibrations above this should show large amplitudes and would not necessarily be well described by an incomplete harmonic basis set sited at one point. It is thus not surprising that some of the vibrational states above the barrier are not well converged. Calculations, employing the close-coupling formalism (for review see [22]) are currently in progress [23]. These might be expected to produce better results for these polytopic states as the potential is analytically integrated over a full basis in the theta internal coordinate.

Table 1 shows that we find the fundamental frequencies of KCN to lie at 302·7 cm^{-1} and 119·7 cm^{-1} for the stretch and bend respectively. These disagree by 10–20 cm^{-1} with those observed by Ismail *et al.* [9] in a matrix isolation study; as we are calculating a gas phase spectrum, better agreement cannot be expected. We find no transition directly comparable to the one at 207 cm^{-1} observed by Leroi and Klemperer [8], however this could possibly be the 02 overtone. It would be interesting to see if further lines could be observed in a repeat of this experiment.

4. ROTATIONAL PROBLEM

Using the vibrational functions calculated in § 3, we calculated the coupling integrals needed for the effective rotational hamiltonian (10). This was done by the same methods used to calculate the integrals needed in the vibrational problem. In a typical case it was found that both types of integral for $m \neq n$ were a hundred or so times smaller than the non-vanishing integral in the case $m=n$. In view of the inaccuracies of the potential of WT, particularly the equilibrium geometry, it was decided that a wavefunction like that given by equation (11) was a sufficiently good approximation. Even though such a wavefunction has the same form as that of a rigid asymmetric top, obtained by solving equation (6), there is an important difference. In the rigid rotor model it is necessary to *assume* a rigid structure, normally the equilibrium geometry; the present approach allows us to take a correct vibrational average of the full inverse effective inertia tensor for each vibrational state.

For a given value of J the set of angular momentum eigenfunctions $|JK\rangle$ is complete. The matrix elements can be evaluated analytically and the results are well known (see for example [12]). We chose to work with a basis of real harmonics which give a real symmetric rather than hermitian secular problem. The matrix elements of the real harmonics, $|JK\cos\rangle$ and $|JK\sin\rangle$, can be obtained from those of the spherical harmonics $|JK\rangle$ using the relationships

$$\left.\begin{aligned} |JK\cos\rangle &= ((-1)^K|JK\rangle + |J-K\rangle)/\surd 2, \\ |JK\sin\rangle &= ((-1)^K|JK\rangle - |J-K\rangle)/\surd 2i. \end{aligned}\right\} \qquad (17)$$

Table 2 compares some of the *ab initio* rotational spectrum with the experimentally assigned lines for the vibrational ground state. Rotational spectra are very sensitive to the geometric parameters of a molecule. The *ab initio* surface of WT has a minimum at $R=2{\cdot}675$ Å and $\theta=105{\cdot}7°$, $r=1{\cdot}157$ Å being held constant; we shall label this geometry I. Thus their surface has a minimum at larger R than observed experimentally [2]; this they attribute to lack of electron correlation in their calculations. Moreover, they worked with an SCF optimized bond length for CN^-, which is shorter than that found experimentally [2] or when extensive configuration interaction is used [24].

A rigid rotor calculation at the experimental geometry [2] gave a spectrum in much better agreement with experiment, especially for the a-type transitions which were now reproduced to within 5 per cent, confirming that it is inaccuracies in the SCF equilibrium geometry of WT which is the major source of disagreement in table 2.

Table 2. Comparison with the rotational spectra of [2] for ground state KCN. I was calculated for the equilibrium geometry of WT [3] and II corresponds to the best experimental geometry [26]. The spectrum of [1] is compared with that calculated using geometry II in table 3.

J'	K'_{-1}	K'_{+1}	J	K_{-1}	K_{+1}	Type	Calculated/MHz I	Calculated/MHz II	Experimental/MHz [2]
3	1	2	3	1	3	a	1798	2366	2423
4	1	3	4	1	4	a	2996	3943	4038
6	1	5	6	1	6	a	6291	8279	8478
7	1	6	7	1	7	a	8388	11038	11303
8	1	7	8	1	8	a	10784	14191	14529
9	1	8	9	1	9	a	13480	17736	18157
10	1	9	10	1	10	a	16474	21673	22185
1	0	1	0	0	0	a	8636	9481	9475
2	0	2	1	0	1	a	17272	18961	18949
3	1	3	4	0	4	b	25917	16041	14443
7	0	7	6	1	6	b	2134	15156	16796
12	2	11	13	1	12	b		24570	19360
3	1	3	2	1	2	a	25459	27852	27817
3	0	3	2	0	2	a	25905	28436	28417
3	2	1	2	2	0	a	25913	28444	28426
3	1	2	2	1	1	a	26358	29035	29028
4	1	4	3	1	3	a	33944	37133	37086
4	0	4	3	0	3	a	34534	37905	37878
4	3	2	3	3	1	a	34548	37930	
4	3	1	3	3	0	a			
4	2	3	3	2	2	a	34545	37924	37887
4	2	2	3	2	1	a	34556	37945	37910
4	1	3	3	1	2	a	35142	38710	38701

We thus decided to perform calculations for geometries based on the experimental minimum. In order to do this within the Eckart framework, it is necessary to shift the potential energy surface, compute a new set of normal coordinates and re-solve the vibrational problem at the new geometry with the new normal coordinates. These vibrational solutions will then have the correct properties for the effective hamiltonian of equation (10).

The potential was shifted by refitting it for geometry I with Hermite polynomials of the dimensionless normal coordinates belonging to the new geometry (Q'_i). The potential of equation (13) is thus rewritten

$$V(R,\theta,r) \simeq V(Q'_1, Q'_2, Q'_3) = \sum_{l=0}^{L} \sum_{m=0}^{M} \sum_{n=0}^{N} a_{lmn} H_l(Q'_1) H_m(Q'_2) H_n(Q'_3). \quad (18)$$

the coefficients a_{lmn} being obtained by Gauss–Hermite integration. $L=14$, $M=9$, $N=2$ was found to give a good representation of the potential. If the refitted potential was used to perform the calculation of table 1, the two fundamentals, ω_1 and ω_2, were changed by only 0·4 cm^{-1} and 1·4 cm^{-1} respectively.

Table 3. Comparison of calculated and experimental spectra in the range 85–107 GHz for the ground and first vibrationally excited state. The experimental lines are from [1] with assignments due to [2]. All transitions are of the *a*-type. All calculations are for geometry II.

						Ground state		First excited state	
J'	K'_{-1}	K'_{+1}	J	K_{-1}	K_{+1}	Calculated/MHz	Experimental/MHz	Calculated/MHz	Experimental/MHz
9	1	8	8	1	7	87044	87005	86120	86080
10	1	10	9	1	9	92762	92621	91707	91439
10	0	10	9	0	9	94468	94360	93439	93538
10	5	5	9	5	4	94833	94567	93788	93421
10	4	6	9	4	5	94842	94643	93797	93514
11	0	11	10	0	10	103835	103706	102708	102479
11	2	9	10	2	8	104684	104587	103519	103379
11	1	10	10	1	9	106347	106285	105219	105152

The refitted potential was then shifted to geometry II. This was the appropriate experimental geometry, $R=2{\cdot}555$ Å, $\theta=98{\cdot}8°$ and $r=1{\cdot}171$ Å obtained by isotopic substitution [7]. A repeat of the vibrational calculation of table 1 with the normal coordinates appropriate to this geometry showed that none of the first 8 band origins changed by more than 2 cm^{-1} and the fundamentals by 0·4 cm^{-1} and 0·1 cm^{-1} respectively.

Part of the calculated rotational spectrum for geometry II is given in table 2. It is clear that, for the *a*-type transitions, good agreement is now obtained. Figure 1 shows approximate directions of the principle axes of inertia for KCN. We note that, although KCN is an asymmetric top, it is very nearly a prolate symmetric top as $I_{aa}^{-1} \gg I_{bb}^{-1} \simeq I_{cc}^{-1}$. The small moment of inertia I_{aa} is dependent almost entirely on the properties of the CN bond. It is this moment of inertia which is sensitively measured by the *b*-type transitions [25]. As we have not attempted a full solution of the vibrational problem and have only represented the CN coordinate by an empirical harmonic potential, one cannot hope to reproduce that part of the rotational spectrum dependent on it. Table 2 shows that there is poor agreement for these *b*-type transitions. However, *b*-type transitions have low intensity and as yet have not been observed for excited vibrational states [26]. The *a*-type transitions are relatively insensitive to the CN geometry and hence there is good agreement between calculated and observed values.

Although many rotational transitions from excited vibrational states have been observed and assigned rotational quantum numbers, no definite assignments to vibrational states has yet been possible [7]. However, our method allows the rotational spectrum of excited vibrational states to be calculated and hence assignments to be made by comparisons with observed spectrum. Table 3 presents one such comparison for the first excited state for the range 85–106 GHz of [1]. A similar comparison for this state with the results of [7] in the range 10–40 GHz also gives good agreement. This confirms that these rotational transitions belong to the first excited state.

Similar comparisons have led to a tentative assignment of the spectrum belonging to the second vibrationally excited state. Table 4 gives calculated

Table 4. Rotational constants for the lowest five vibrational states calculated using geometry II.

State	A/MHz	B/MHz	C/MHz
1	59 860·59	4 937·87	4 543·60
2	63 234·24	4 887·05	4 490·03
3	64 752·44	4 889·99	4 477·14
4	59 702·58	4 927·55	4 528·18
5	64 645·54	4 900·17	4 475·90
Experimental†	58 265·81	4 940·055	4 536·214

† Experimental ground state value from [2].

rotational constants for the lowest 5 vibrational states. It is clear that the calculated rotational constants, and hence spectra, are very similar for the second and fourth vibrationally excited states, states 3 and 5 in table 4. This means that any assignment of these states can only be tentative.

5. Conclusions

In this paper we have successfully applied the Whitehead–Handy method to the low lying vibrational states of KCN and hence obtained a rotational spectrum for these states. This method relies on being able to define an equilibrium structure for the molecule and thus is not appropriate for the higher vibrational states where polytopic [5] motion is to be expected. However, for states of large amplitude, separation of vibrational and rotational problems can no longer be such a good approximation. In a future paper [23] we hope to explore the high amplitude vibrations in the bending coordinate more fully by using a method [22] which integrates analytically over this coordinate with no assumptions about equilibrium structures or separability. However, for the low-lying states our vibrational calculations are well converged and when a realistic equilibrium geometry is used good agreement is obtained with the experimental rotational spectrum. This has allowed vibrational assignments to be made to the rotational spectrum of vibrationally excited states.

The main problem in this *ab initio* calculation of vibrational and rotational spectra has been the accuracy of the *ab initio* surface and more particularly the location of the *ab initio* minimum. Wormer and Tennyson [3] give the time to calculate one potential point as 6 hours on an IBM 370/158. By comparison the calculation with $M_A=9$, $M_B=6$ of table 1 took 70 minutes, the integration over vibrational states of equation (10) took 10 minutes per vibrational state and calculation of a rotational spectrum with $J \leqq 11$ took 6 seconds, all timings on the same computer facility. Thus the calculation of the *ab initio* potential points is the major expense in an *ab initio* dynamical study such as this. Better dynamical results can only be obtained by using more accurate, and more expensive, *ab initio* potential energy calculations.

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